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ELECTRO-OPTICAL SYSTEMS, INC. Pasadena, California

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RESEARCH AND INVESTIGATION OF MATERIALS FOR
LASER APPLICATIONS

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ABSTRACT

The work reported for this period consists of the following: the synthesis and purification of selected beta-diketone derived chelates using different radicals, the results of fluorescence and decay time measurements on some of these compounds, the effect of halogenation and purity of sample on the above measurements, and the development of new glass hosts and the successful lasering of a sample of this glass doped with neodymium.

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1. INTRODUCTION

The objective of this program is to prepare and characterize optimized solid state materials for laser applications. Our approach is based primarily on metal-organic materials, plastics, and glasses where the plastics and glasses are used as a host material for metal-organic molecules and rare-earth ions. This work has been divided into a survey part where a large number of possible materials were synthesized and characterized and a second part where the more promising materials were to be studied more intensively.

During the past quarter, the chelate synthesis portion of the work has been directed towards those compounds which will be used as the basis of a more intensive study. The ligands are beta-diketones derivatives where different radicals are used in order to investigate the influence of the radicals on the fluorescence, decay time, and quantum efficiency. Thus we have synthesized the acetylacetonates, the trifluoroacetonates, the hexafluoroacetonates, and the thenoyl trifluoroacetonates. The fluorescence emission and decay time measurements of these compounds are in progress and some of these results are presented.

The work on glass hosts during this period has consisted of the following. A barium potassium, high silica glass host has been developed which shows high fluorescence when doped with neodymium and erbium. The fluorescence emission and decay times of these materials is presented in this report. The successful lasering of a sample of the neodymium-doped material when fabricated into a laser rod is reported. Also, the development of a new glass host showing approximately a three-fold increase in fluorescence over the above glass when doped with neodymium is discussed.

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2. RARE EARTH CHELATES

2.1 Synthesis

During this period nine rare earth chelates were synthesized and are listed below. Difficulties were encountered when performing the reaction in non-aqueous solution. The compounds produced from non-aqueous solutions usually had wide melting point ranges and poor yields. It was decided to try another method whereby the ligand compound is reacted with the rare earth compound in an aqueous solution as described by Holtzclaw[1] and Belford, et al[2]. Utilizing the latter method, higher yields and narrower melting point ranges were realized. The following describes the syntheses of each compound in greater detail.

2.1.1 Acetylacetone Adducts of Neodymium and Erbium

$$3 \ CH_3\overset{O}{\underset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\underset{\|}{C}}\text{-}CH_3 \quad \xrightarrow{MCl_3} \quad \left[CH_3\text{-}\overset{O\cdots M\cdots O}{\underset{\|}{C}}\text{-}CH\text{=}\overset{}{\underset{\|}{C}}\text{-}CH_3 \right]_3 + 3HCl$$
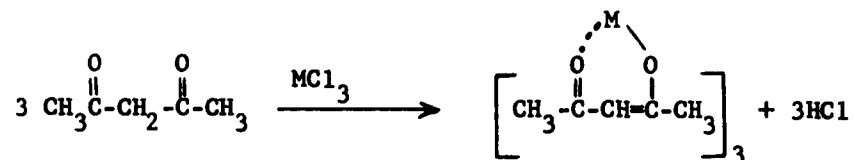
Solutions of $NdCl_3$ and $ErCl_3$ in methanol were each reacted with solutions of acetylacetone in piperidine-methanol at room temperature. The solvent was evaporated under reduced pressure and the reaction product extracted from the piperidine hydrochloride with toluene. The products obtained were recrystallized several times from toluene-hexane to give the neodymium tris-acetylacetonate compound melting point 136-140°C and erbium tris-acetylacetonate melting point 146-155°C.

1. Holtzclaw, Johnson, and Hengeveld, J. Am. Chem. Soc., 74, 3776 (1952).
2. Belford, Martell, and Calvin, J. Inorg. Nuclear Chem., 2, 11 (1956).

2.1.2 Synthesis of Neodymium Tris-Ethylacetoacetate

$$3 \ CH_3CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \quad \xrightarrow{MCl_3} \quad \left[CH_3CH_2-O-\overset{M}{\underset{O\ \ \ \ \ O}{\overset{\|}{C}}}-CH=\overset{}{C}-CH_3 \right]_3 + 3HCl$$
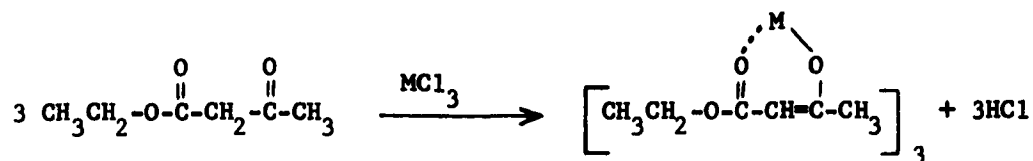
       The method employed was as described in Section 2.1.1.
The product obtained was recrystallized several times from toluene-
hexane to give the neodymium tris-ethylacetoacetate compound melting
point 208-210°C.

2.1.3 4,4,4-Trifluoro-1(2-Thienyl)-1,3-Butanedione Adducts of Praseodymium, Erbium, Samarium, and Terbium

$$3 \ \underset{S}{\bigcirc}\!-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CF_3 \quad \xrightarrow{MCl_3} \quad \left[\underset{S}{\bigcirc}\!-\overset{M}{\underset{O\ \ \ \ O}{\overset{\|}{C}}}-CH=\overset{}{C}-CF_3 \right]_3 + 3HCl$$
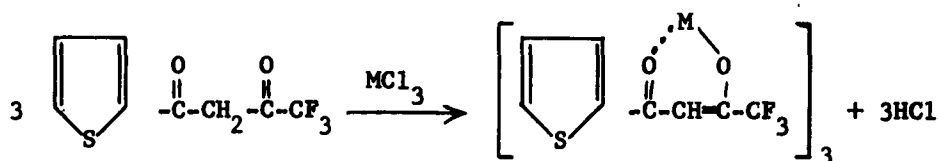
       Solutions of $PrCl_3$, $ErCl_3$, $SmCl_3$, and $TbCl_3$ in methanol
were each reacted with solutions of the thienyl compound in piperidine-
methanol at room temperature. The solvent was evaporated under reduced
pressure and the reaction product extracted from the piperidine hydro-
chloride with benzene. The products obtained were recrystallized several
times from ether-pentane to give the praseodymium-thienyl compound melt-
ing point 151-154°C, the erbium-thienyl compound melting point 159-161°C,
the samarium-thienyl compound melting point 122-129°C, and the terbium-
thienyl compound melting point 122-129°C.

2.1.4 Syntheses of Samarium and Terbium Tris-Trifluoroacetyl-acetonate

$$3 \ CF_3\text{-}\overset{\overset{\text{O}}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\text{O}}{\|}}{C}\text{-}CF_3 \quad \xrightarrow{MCl_3} \quad \left[CF_3\text{-}\overset{\overset{\text{O}}{\overset{\|}{}}}{C}\text{-}CH\text{=}\overset{\overset{\text{O}}{|}}{C}\text{-}CF_3 \right]_3 + 3HCl$$
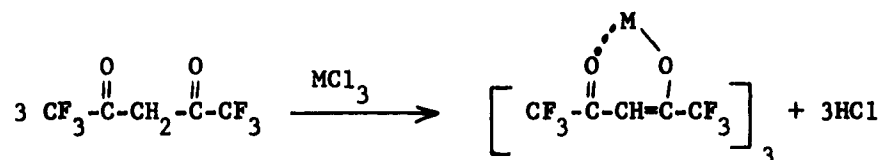
A trifluoroacetylacetone-methanol solution was added to an aqueous samarium chloride solution and heated on a steam bath. An appropriate amount of potassium carbonate was added and reaction allowed to continue. The product obtained was extracted with ether and recrystallized several times from benzene-carbon tetrachloride to give the samarium tris-trifluoroacetylacetonate compound melting point 129-132°C.

The terbium tris-trifluoroacetylacetonate was prepared from an aqueous solution as described above, however, ammonium hydroxide was used in place of potassium carbonate. It was not necessary to heat the reaction mixture. The product was recrystallized several times from ether-hexane to give the terbium tris-trifluoroacetylacetonate compound melting point 135-137°C.

2.2 Purification and Analysis

Impurities in the rare earth chelates can take several forms:

(1) Unreacted starting materials: MX_3, the rare earth halide; C, the unreacted chelating compound.

(2) Compounds related to the desired product but differing in number of ligands combined to the metal. (MC_2X when MC_3 is desired.)

The problem of purification must be preceded by the precise determination of the purity of the sample so that a quantitative measure of contamination can be obtained.

Due to the complexity of the chelate molecules, the standard techniques cannot generally be applied and because of the purity necessary due to the, as yet, undetermined requirements of spectroscopy, the usual criteria of organic chemistry purity are used only for qualitative measurements.

Accordingly, the first measure of the purity of a newly synthesized compound is its melting point. Since for any compound the presence of a second material as a contaminant lowers the melting point, the first criterion which is applied is successive recrystallization until a constant melting point is obtained.

Following multiple recrystallizations, the compounds are subjected to high vacuum treatment either to remove occluded ligand or, in the case of volatile compounds, to provide purification by fractional vacuum sublimation. When treated thermally, in vacuo, purification of the chelates were obtained. Many chelates gave small amounts of sublimate which proved to be ligand starting material. In almost all cases fluorescence intensities were enhanced; the measured increments were, generally, less than 20 percent and were not considered to be significant. Neodymium acetylacetonate, on the other hand, upon heating to 130°C for 2.5 hours, showed an increase in fluorescent intensity by a factor greater than two.

The determination of the colligative properties of solutions give a measure of the molecular weight of the substance. When using ebullioscopic, as well as other colligative methods, reliable results are obtained only when the molecular weight is such that sufficient numbers of particles are in solution to provide an appreciably measurable effect. Hence, a molecular weight in the neighborhood of 500 is the upper practical limit for this type of measurement with the equipment presently in use.

A second technique applicable to all compounds is elemental analyses for the constituent elements. Samarium tris-dibenzoylmethide,

having a theoretical metal content of 18.35 w/o, has been found to have 17.74 w/o samarium. Terbium tris-trifluoroacetylacetonate, having a stoichiometric metal content of 25.67 w/o and an observed metal content of 24.6 w/o. Four separate samples of neodymium acetylacetonate prepared gave the following metal contents upon analysis: 33.6, 33.9, 36.0, 30.1 w/o. The theoretical values for $Nd(AA)_3$ is 32.69 w/o. Hence, the first two samples are pure tridentate material, the third appears to be a mixture of bi- and tri-dentate material, and the last sample seems to have some excess ligand. Neodymium ethylacetoacetate, theoretically 27.15 percent metal, analyzed to be 28.6 percent neodymium, indicating tridentate material. Most of these results are within the experimental error of the analytical procedure so that it appears that the compounds synthesized consist predominantly, if not completely, of the desired tridentate material.

In view of the high degree of purity which may be required to obviate impurity quenching, the approaches described above are not sufficiently sensitive. However, chromatographic techniques may be successful. Attempts at vapor phase chromatography met with failure due to the low degree of volatity giving thermal decomposition before vaporization could occur. Experimental use of liquid phase chromatography using ceramic substrates and paper substrates is currently under investigation. It is anticipated that the sensitivity of chromatography should be invaluable in the determination of both the number of species present and their relative amounts. Furthermore, this approach offers the most promising way to separate a given preparation into its components.

3. SPECTROSCOPY OF MATERIALS

3.1 Fluorescence Spectra of Rare Earth Chelates

The fluorescence emissions of six rare-earth chelates were measured as a function of wavelength. The chelates studied were samarium tris-trifluoroacetylacetonate $Sm(TAA)_3$, samarium tris-hexafluoroacetylacetonate $Sm(HAA)_3$, terbium tris-trifluoroacetylacetonate $Tb(TAA)_3$, neodymium tris-acetylacetonate $Nd(AA)_3$, praseodymium tris-thenoyl trifluoroacetonate $Pr(TTA)_3$, and erbium tris-thenoyl trifluoroacetonate $Er(TTA)_3$.

The first four of these rare-earth chelates were examined for fluorescence at both $300^\circ K$ and $77^\circ K$. The last two were observed only at $300^\circ K$. Strong fluorescence was observed from $Sm(HAA)_3$, $Sm(TAA)_3$, and $Tb(TAA)_3$. Only weak emissions occurred in the cases of neodymium and praseodymium, and no fluorescence in the case of erbium. The fluorescence spectra will be discussed in some detail after the following brief description of the apparatus used in making the observations.

The rare-earth chelates were excited with illumination from a Hanovia 612C Hg arc lamp. A Corning CS-737 filter was placed in the optical path to absorb the emission from the Hg arc at wavelengths longer than 3900 Å. (Measurements of the transmission of the Hg spectrum through the Corning filter showed, however, that some light was passing through the filter at approximately 7500 Å. No other long wavelength transmission through the filter was observed.) After filtering, the light was focussed on the sample. This illumination, limited by the filter, consisted essentially of the Hg spectrum in the region from 3100 Å to 3900 Å, and served to excite the chelates and produce the observed fluorescence.

The fluorescence emission was focussed on the entrance slit
of a Perkin-Elmer Model 112 single-beam double-pass spectrometer. The
optical arrangement from the Hg source to the spectrometer entrance
slit was as shown in Fig. 3.1. A flint glass prism was used in the
spectrometer, and an S-1 photomultiplier was used as a detector in the
visible region of the spectrum. When measurements were made in the
near infrared region, a PbS cell was used in place of the photomultiplier.

The sample holder consisted simply of an oblong block of stain-
less steel, 1" long by 1/2" wide by 1/4" thick, into which a slot 1/8"
wide by 5/8" long by 1/32" deep was milled. The slot was centrally
located on one of the 1" by 1/2" flat faces, and a powder sample of
the rare-earth chelate was loaded into the slot and subsequently held
in place by a quartz flat affixed to the face of the steel block. For
fluorescence measurements the sample holder was mounted such that the
slot containing the sample was in a vertical position.

The emission spectra of the six rare-earth chelates mentioned
in the opening paragraph of this section were recorded on a Leeds and
Northrup Speedomax G recorder, and are shown in Figs. 3.2 thru 3.10.
Only those portions of the spectra in which emission occurred are repro-
duced in the figures. The wavelengths of the emissions, and qualitative
indications of intensities, are listed in Table 3.1. In the cases of
$Sm(TAA)_3$, $Sm(HAA)_3$, $Tb(TAA)_3$, and $Nd(AA)_3$, data were taken at both $300^{\circ}K$
and $77^{\circ}K$. By referring to Figs. 3.2 and 3.4 it may be observed that
the fluorescence of the samarium hexafluoro chelate is stronger than
that of the samarium trifluoro chelate. (Note that the slit widths are
different in the two runs.) It may be inferred that the effect of the
halogenation is to reduce the non-radiative losses. We plan to extend
these measurements to ligands using other radicals in order to determine
the extent to which the non-radiative losses can be reduced.

It may be observed by referring to Figs 3.2 to 3.7 that some
of the emission bands are stronger at liquid nitrogen temperature, but

TABLE 3.1   OBSERVED FLUORESCENCE EMISSION OF RARE
EARTH CHELATES.

VW = Very Weak   M = Medium   VS = Very Strong
W = Weak   S = Strong

CHELATE	EMISSION WAVELENGTH, Å	RELATIVE INTENSITY	TEMP. °K
$Sm(TAA)_3$	9550	VW	77
	6560	M	77
	6080	W	77
$Sm(HAA)_3$	9570	M	77
	9175	W	77
	8950	W	77
	6540	VS	77
	6100	S	77
	6025	M	77
$Tb(TAA)_3$	6615	W	77
	6230	M	77
	5890	M	77
	5810	M	77
	5462	VS	77
	5428	VS	77
$Nd(AA)_3$	9025	W	77
$Pr(TTA)_3$	6160	VW	300
$Er(TTA)_3$	Dead		300

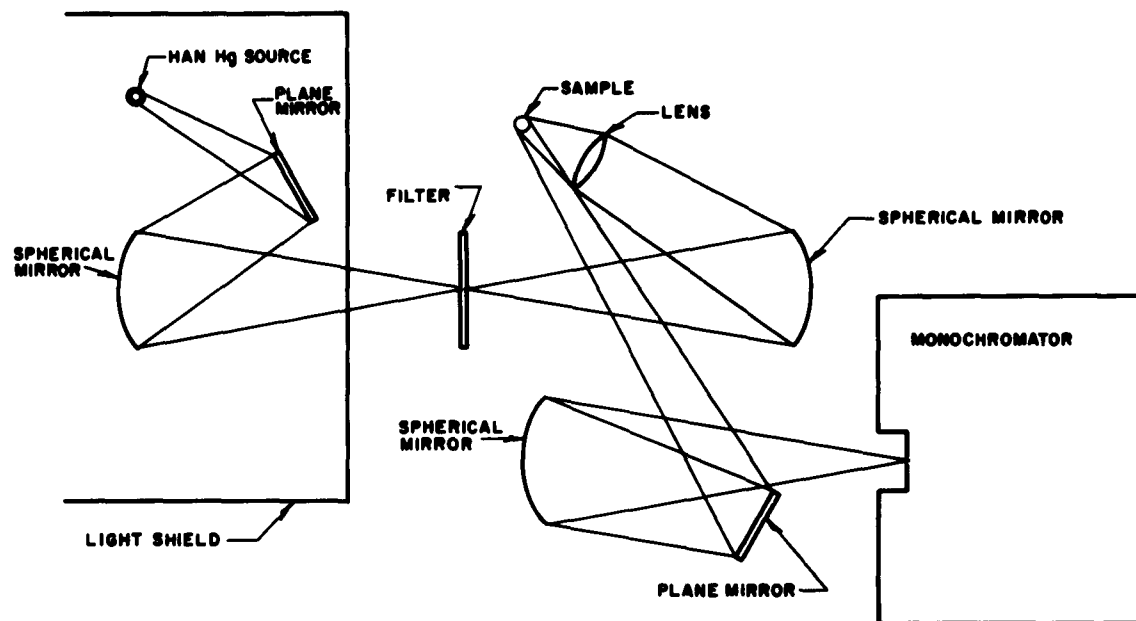FIG. 3.1 SCHEMATIC OF OPTICAL TRAIN FOR OBSERVING FLUORESCENCE EMISSION

FIG. 3.2   FLUORESCENCE SPECTRUM OF Sm(HAA)₃ AT 77°K.
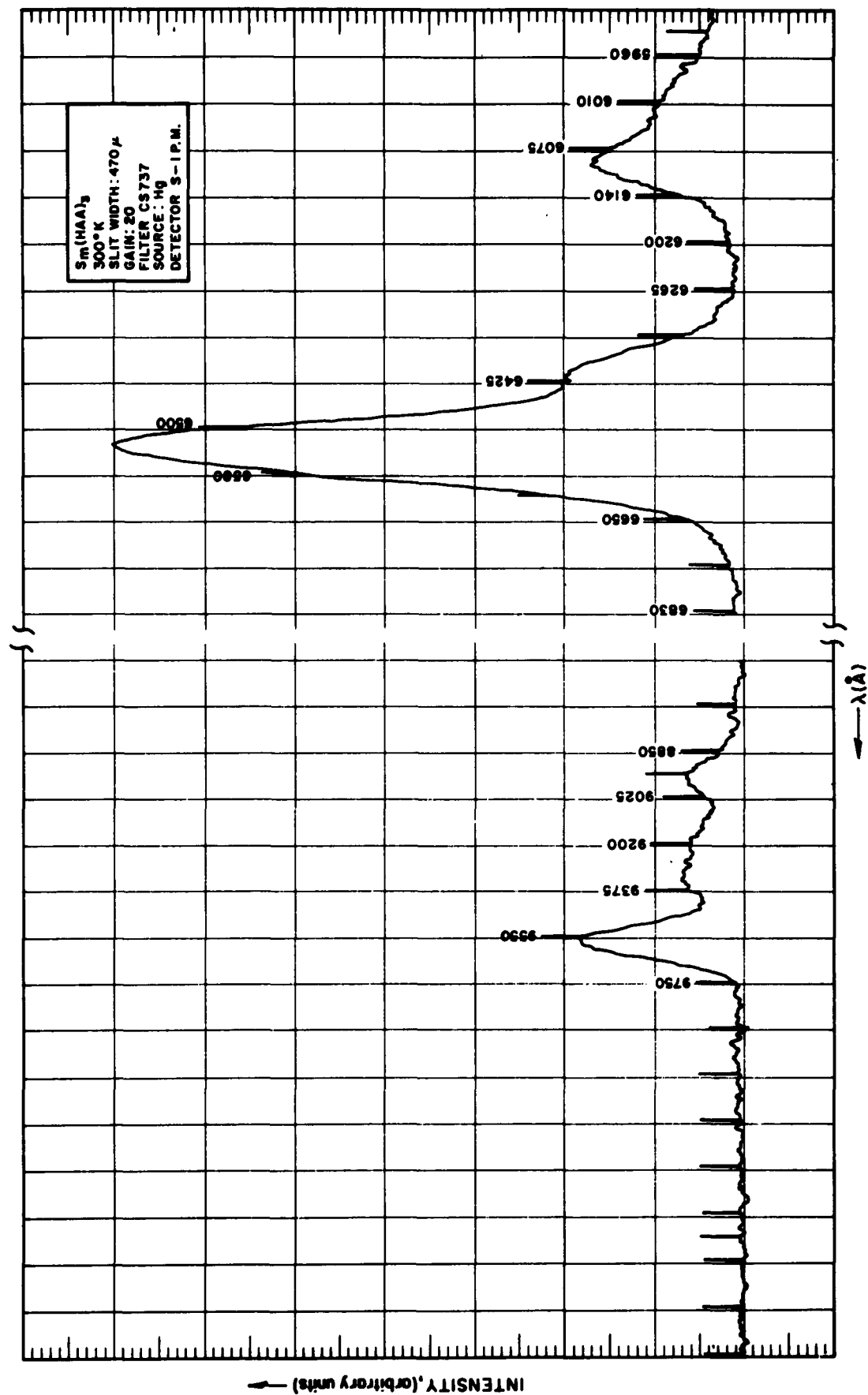
FIG. 3.3 FLUORESCENCE SPECTRUM OF Sm(HAA)$_3$ AT 300°K.

Sm(HAA)$_3$
300°K
SLIT WIDTH: 470 μ
GAIN: 20
FILTER CS737
SOURCE: Hg
DETECTOR S–I.P.M.

INTENSITY, (arbitrary units)

λ(Å)
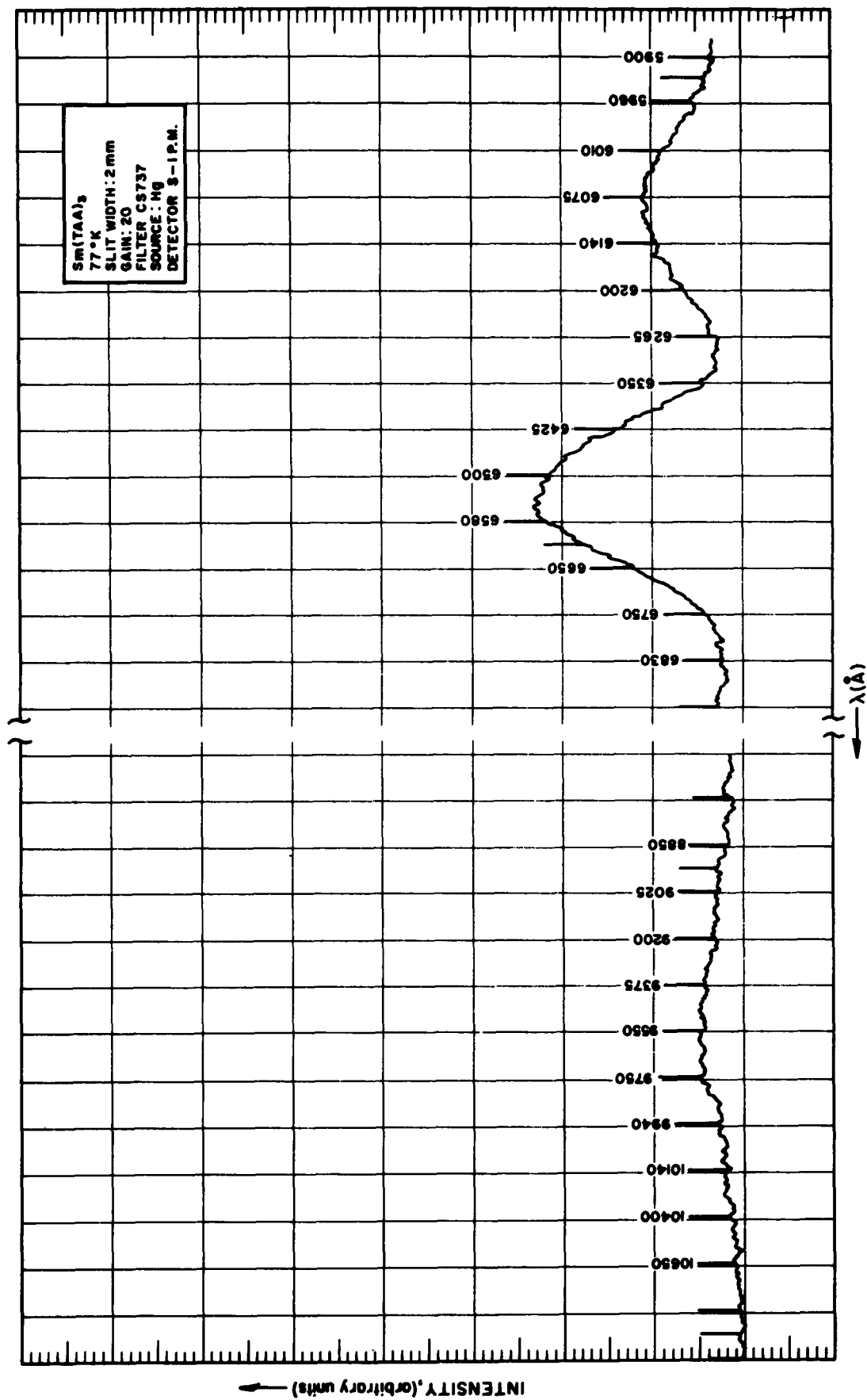
FIG. 3.4   FLUORESCENCE SPECTRUM OF Sm(TAA)$_3$ AT 77°K.

Sm(TAA)$_3$
77°K
SLIT WIDTH : 2 mm
GAIN : 20
FILTER CS737
SOURCE : Hg
DETECTOR S—I.P.M.

INTENSITY, (arbitrary units)

λ(Å)

5900 5960 6010 6075 6140 6200 6265 6350 6425 6500 6560 6650 6750 6830

8850 9025 9200 9375 9550 9750 9940 10140 10400 10650

FIG. 3.5   FLUORESCENCE SPECTRUM OF Sm(TAA)₃ AT 300°K.

Sm(TAA)₃
300° K
SLIT WIDTH: 2 mm
GAIN: 20
FILTER: CS 737
SOURCE: Hg
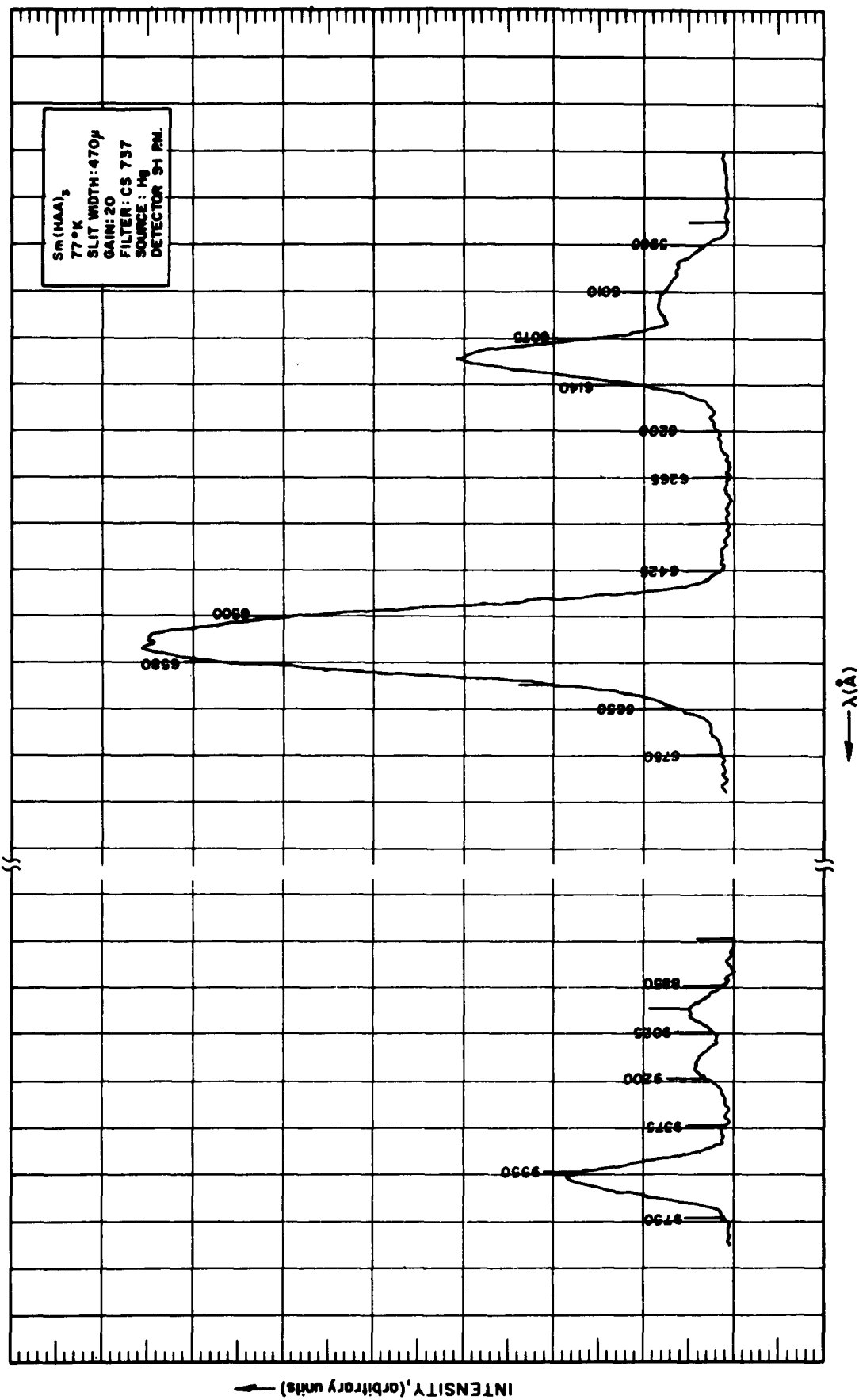DETECTOR: S–1 P.M.

Axis labels: λ(Å) ; INTENSITY, (arbitrary units)

FIG. 3.6 FLUORESCENCE SPECTRUM OF Tb(TAA)$_3$ AT 77°K.
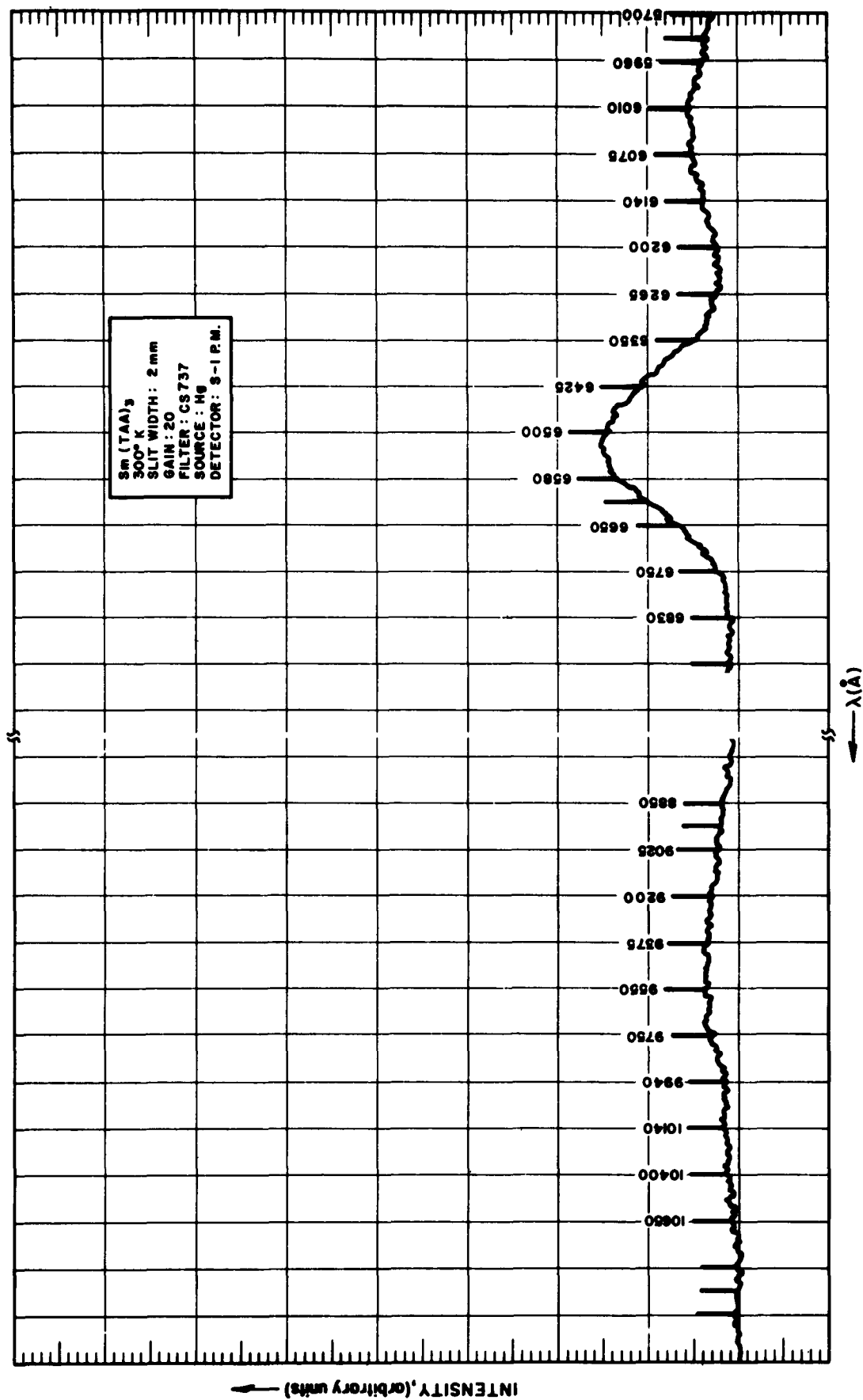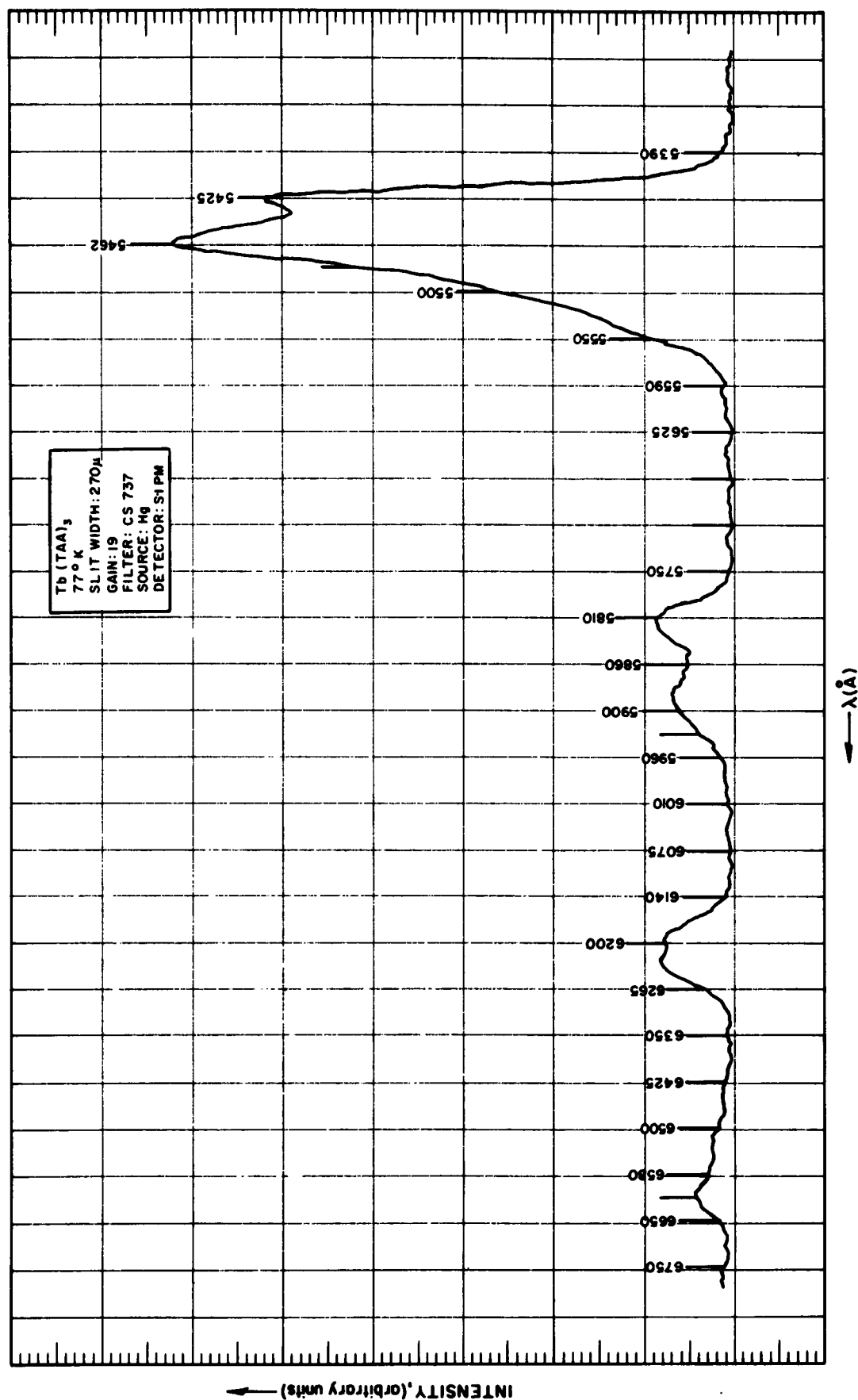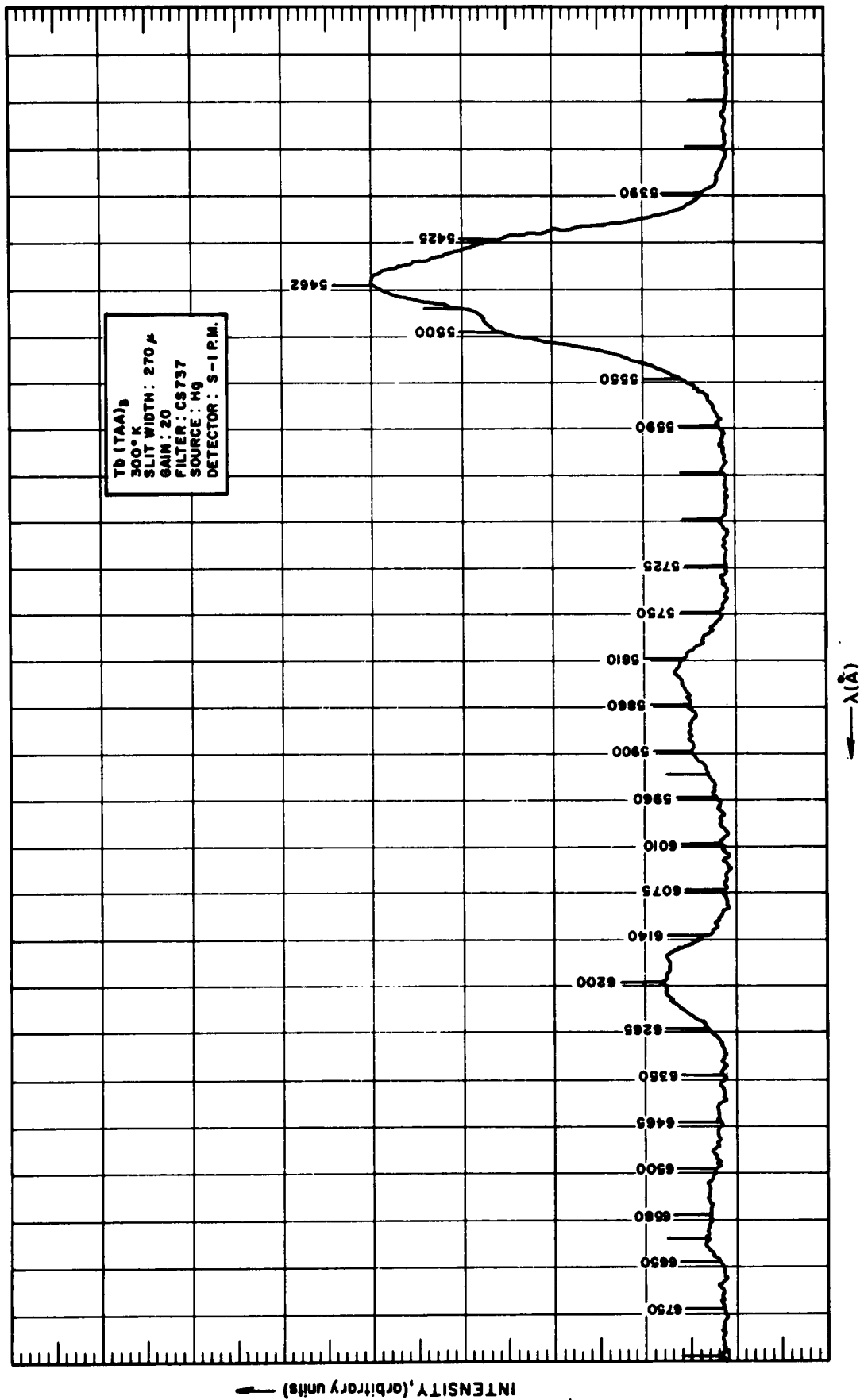
FIG. 3.7 FLUORESCENCE SPECTRUM OF Tb(TAA)$_3$ AT 300°K.
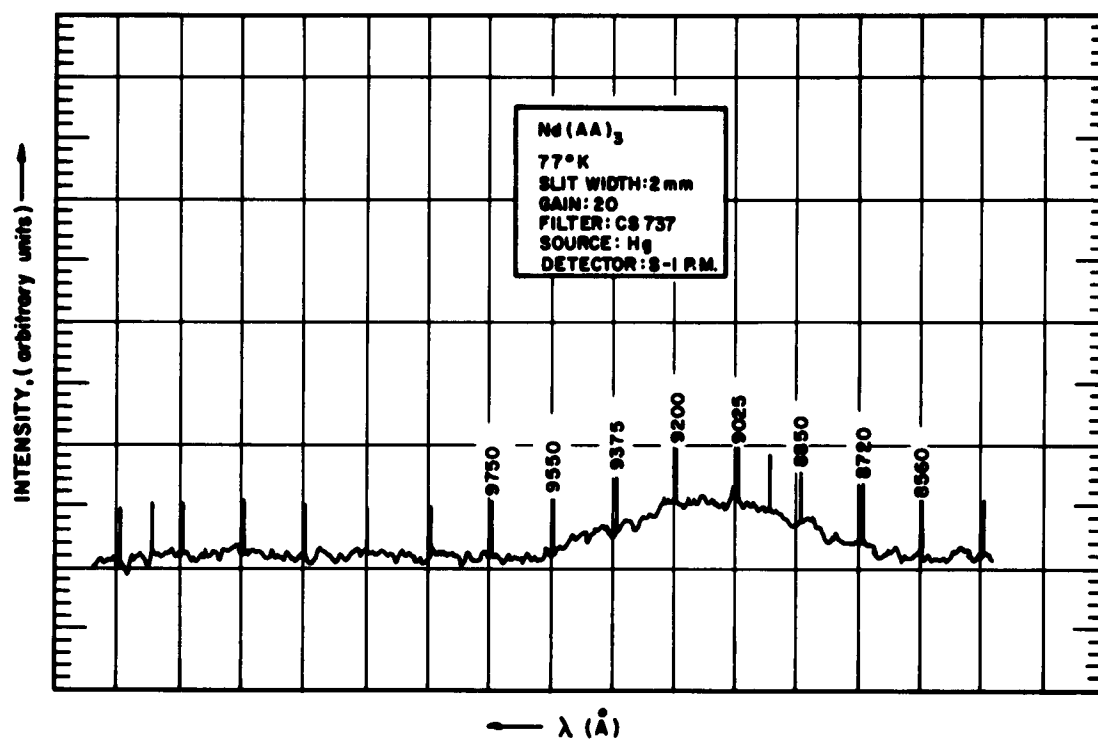
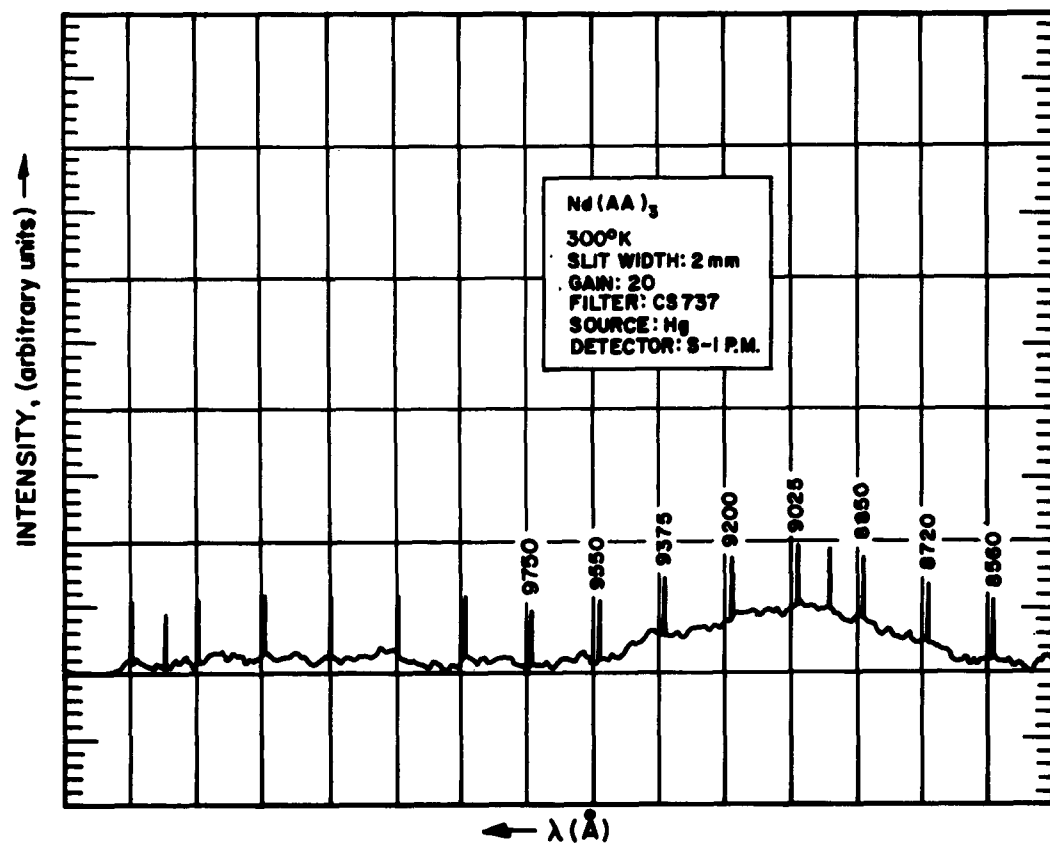FIG. 3.8   FLUORESCENCE SPECTRUM OF Nd(AA)$_3$ AT 77°K.
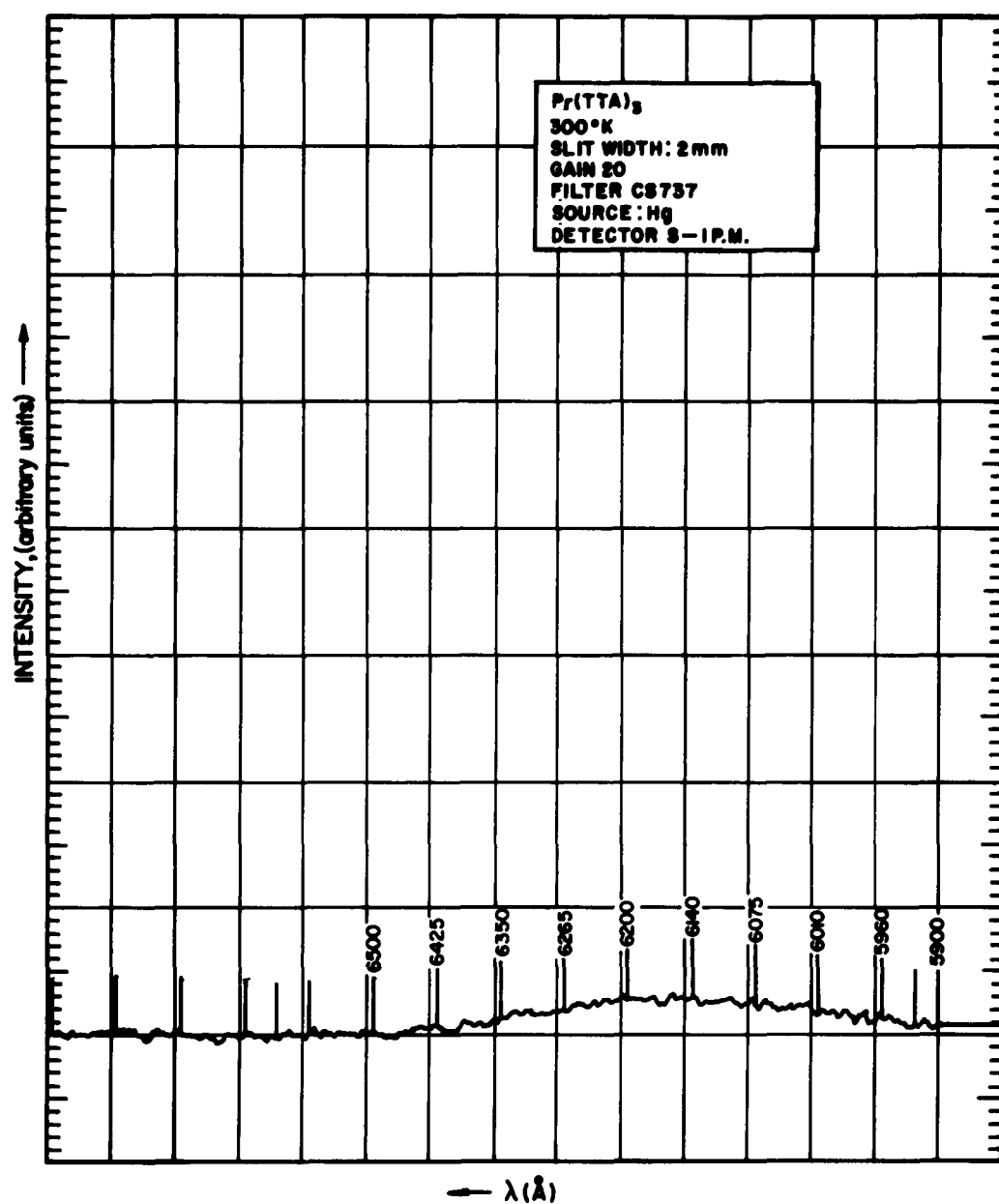
FIG. 3.9   FLUORESCENCE SPECTRUM OF Nd(AA)$_3$ AT 300°K.

FIG. 3.10   FLUORESCENCE SPECTRUM OF Pr(TTA)$_3$ AT 300°K.

that is not true for all of the bands recorded. Also, in some cases, but not all, the lower temperature results in a narrower line. It is believed that the inconsistencies in these effects may in part be attributed to insufficient purity. Attempts are being made to improve the purity of the samples by improving the synthesis techniques as well as the purification processes.

The Corning CS-737 filter used in these experiments transmits in the ultraviolet region of the spectrum, from 3100 $\overset{o}{A}$ to 3900 $\overset{o}{A}$. The maximum transmission, 30 percent, occurs at 3600 $\overset{o}{A}$, according to the Corning data. Now the absorption of $Sm(TTA)_3$, $La(TTA)_3$, $Eu(TTA)_3$, and $Tb(TTA)_3$ in this spectral region have been determined by Kuhlman (Ref. 3), whose data are reproduced in Fig. 3.11. It was observed by Kuhlman that the absorption was independent of the rare-earth ion, and that the rare-earth TTA chelates had absorption characteristics differing only slightly from that of TTA itself. The $R(TTA)_3$ absorption characteristic given in Fig. 3.11 may be expected to hold also for the $Er(TTA)_3$ and $Pr(TTA)_3$ chelates reported upon here.

We have measured the molar absorption coefficient of $Nd(AA)_3$ in these laboratories over the same wavelength interval, and the results are presented in Fig. 3.11 with Kuhlman's data for $R(TTA)_3$. It will be observed that the peak absorption for the AA ligands is four times that of the TTA, but that this peak occurs at shorter wavelengths. In the pump region used in the fluorescence measurements just presented, the absorption of the AA is less than that of TTA. However, the molar absorption coefficients for these materials are so high that even in the pump region from 3100 $\overset{o}{A}$ to 3800 $\overset{o}{A}$ essentially all of the incident radiation is absorbed in a shallow region close to the surface of the microcrystals used for the fluorescence measurements. For example, it may easily be determined, using the Beer-Lambert relation, and referring to Fig. 3.11, that for the $Nd(AA)_3$ chelate at 3420 $\overset{o}{A}$, where

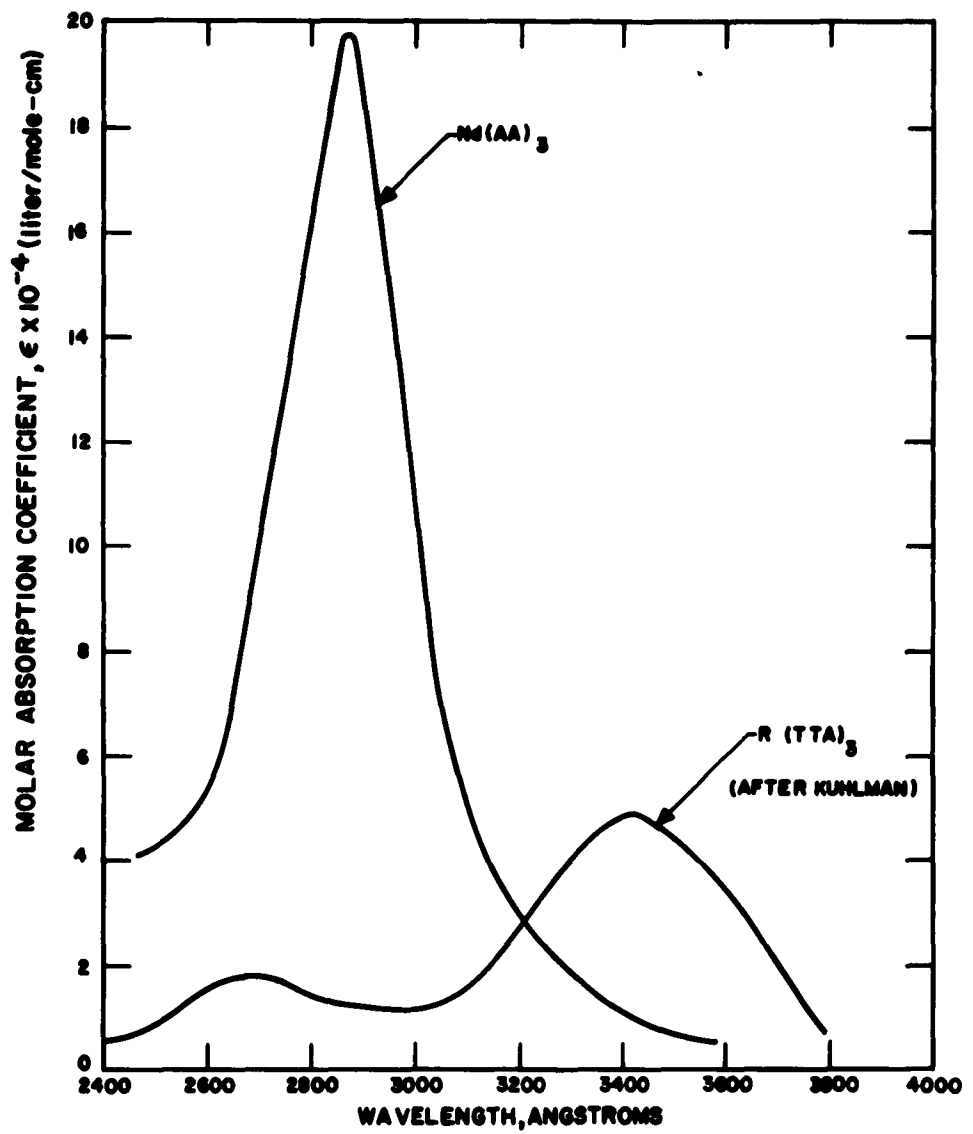3. C. W. Kuhlman, Jr., "Kinetics of Luminescence of Some Rare Earth Compounds," Ph.D. Thesis, Washington Univ. (1953).

FIG. 3.11   MOLAR ABSORPTION COEFFICIENTS OF RARE
EARTH CHELATES

$\mathcal{E} = 10^4$ liter/mole-cm, that 90 percent of the 3420 $\overset{o}{A}$ radiation will be absorbed in the chelate within 1.0 micron of the surface of the micro-crystal. Therefore, failure to observe appreciable fluorescence in the case of $Nd(AA)_3$ cannot be attributed to insufficient pumping of the chelate molecule.

3.2 Fluorescence Decay Times

Fluorescence decay times were made by the apparatus described previously. The method consists essentially of recording the decay curve on an oscilloscope after pumping with an intense flash of short duration. Decay times longer than the pump duration (i.e., approximately 5 μsec.) can thus be observed. Photographs of the oscilloscopic trace showing the decay are given in Fig. 5.4 in the section on glasses.

Measurements of the lifetimes were made for the glasses as described in that section and are being made for the beta-diketone derivatives using different radicals. It is believed that halogenation of the radicals will reduce the non-radiative losses in the chelates. To date measurements have been made on terbium trifluoroacetylacetonate and on a number of neodymium chelates. A decay time of 400μ seconds was obtained for the terbium chelate but the fluorescence intensity was not sufficiently intense to obtain results for the neodymium chelates. The decay times of the samarium chelates will be made during the following period. The decay time of Tb^{+3} in trifluoroacetylacetonate (trace shown on Fig. 5.4(d) of approximately 400μ seconds seems to be quite low in comparison with that in acetylacetonate which was previously reported as approximately 700μ seconds in view of the above considerations on halogenation. One possible reason for the observed short decay time may be the presence of impurities. Therefore, attempts are being made to further purify and characterize this compound as well as the other halogenated compounds.

4. PLASTIC HOST MATERIALS

Synthesis of new rare earth chelates required the development of a plastic which will have better ultraviolet transparency. Methyl methacrylate and other derivatives of acrylic acid are much better for use in ultraviolet application than epoxies.

The use of external mirrors eliminated the problem of the end mirrors on the epoxy resin rods. Also, it was decided to increase the length of the epoxy resin laser rods in order to decrease the effects of the end losses and to make possible higher power levels. The laser rods were made four to six inches long. The cladding was changed to Vycor capillary because of the difficulty of fabricating methyl methacrylate cladding of this length. The ends of the capillary were capped with the doped epoxy resin and optical flats were made on the epoxy resin ends. The expansion coefficient of epoxy resin is much larger than that for Vycor. This created a problem especially when these samples were cooled to liquid nitrogen temperatures and also when thermally shocked on flashing.

The absorption edge of the epoxy resin as described in previous reports is not far from the absorption region for the chelates such as benzoylacetonate, but completely overlaps the pump region for the newer chelates which have been synthesized, such as the ethylaceto-acetate. This has led us to seek other plastics. We have found that it is possible to dope the acrylate plastics such as methyl metha-crylate, etc., with the chelates without quenching their emission.

This is done by dissolving the acrylate plastic in a solvent with the chelate. The solvent is removed by vacuum evaporation and the residue ground to a powder. The powder is then molded by the

application of pressure and heat into a clear plastic. A special
mold has been designed and constructed to carry out this procedure.
Using this mold, disks of the doped plastic will be prepared and rods
one-fourth inch in diameter and four inches long will be fabricated.
These rods will be investigated for suitability as host material.

5. GLASSES

Work on the glass was continued in order to find high efficiency glass host material, using Nd^{+3} as the laser ion, and then extending this host on other rare earths. The approach to this problem consists of determining the most suitable compound form in which to introduce the rare earth dopand and to develop a suitable formulation of the glass host.

As discussed previously, neodymium was introduced into glass in different compound forms. The glass matrix used was of the barium potassium silicate type and was developed on this program. The neodymium was introduced into this matrix in the form of $NdCl_3$, Nd_2O_3, NdF_3, and $Nd_2(MoO_4)_3$. It was found that NdF_3 gives the highest fluorescence emission and the longest decay time. Fig. 5.1 and Fig. 5.2 gives relative comparison of fluorescence emission for 0.5 percent neodymium doped calcium tungstate and 2 percent neodymium fluoride doped barium potassium silicate glass which we shall designate as glass matrix No. 3. Fig. 5.1 gives the results for wide slit width where the total emission can be compared. It can be seen that the emission for the glass sample is about three-fourths of that for the tungstate. Fig. 5.2 gives the emission for a narrower slit width where the half-width of the emission band can be seen to be about 250 Å. The slit width is not sufficiently narrow to show the line width of the tungstate which is about 40 Å.

During this period we have sought other glass hosts in an effort to improve the fluorescence intensity. It is believed that a glass host which is more nearly crystalline would be a more suitable host material from the point of view of line width and fluorescence intensity. For this reason the formulation of our glass host (i.e., glass No. 3)
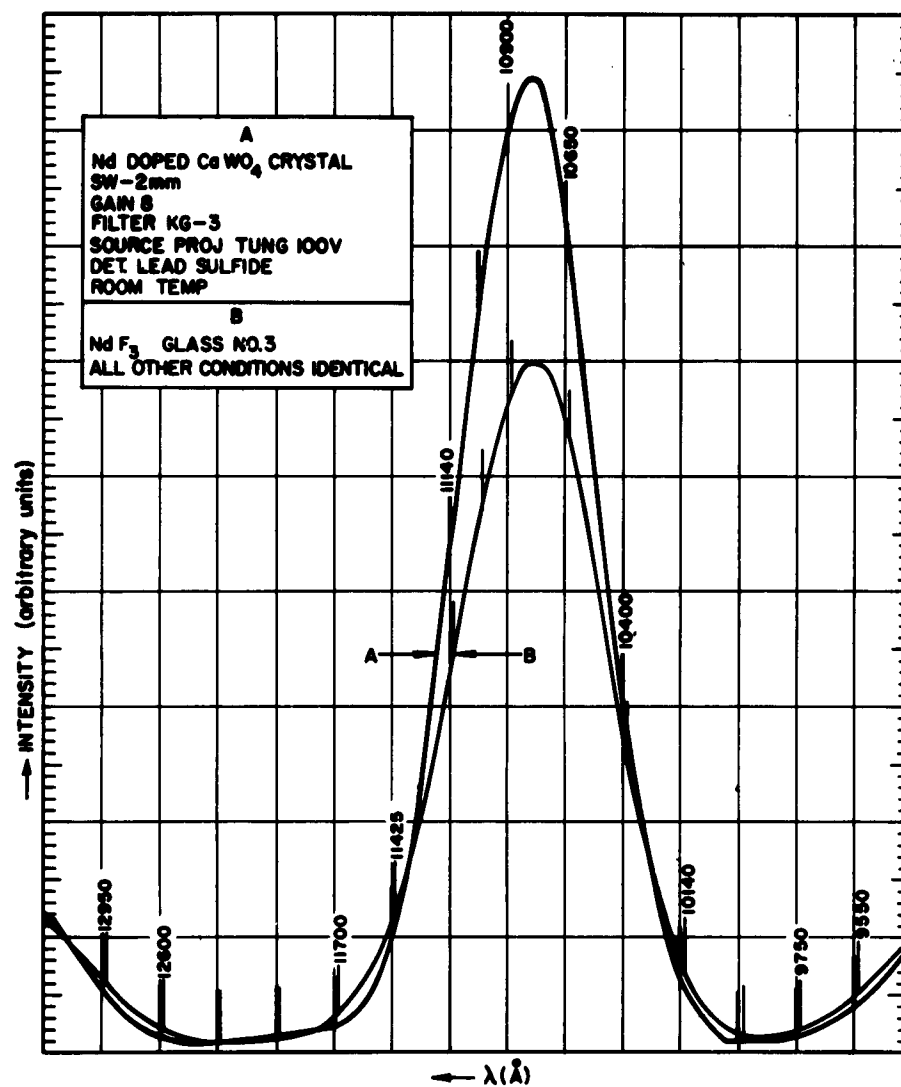
FIG. 5.1   EMISSION OF Nd^{+3} IN GLASS AND $CaWO_4$ CRYSTAL
MATRICES - SLIT WIDTH 2 MM.

INTENSITY (arbitrary units)

A
SiO$_2$(60%)-BaO-BaF$_2$ - NdF$_3$ GLASS ROD
SW 115 μ
GAIN 19
FILTER KG3-CS497
SOURCE PROJ TUNG 100V
DET. LEAD SULFIDE
GAIN FACTOR PER STEP=1.65

B
Nd DOPED Ca WO$_4$ CRYSTAL
SW 115 μ
GAIN 20
FILTER KG3-CS497
SOURCE PROJ TUNG. 100V
DET. LEAD SULFIDE
GAIN FACTOR PER STEP=1.65

λ (Å)
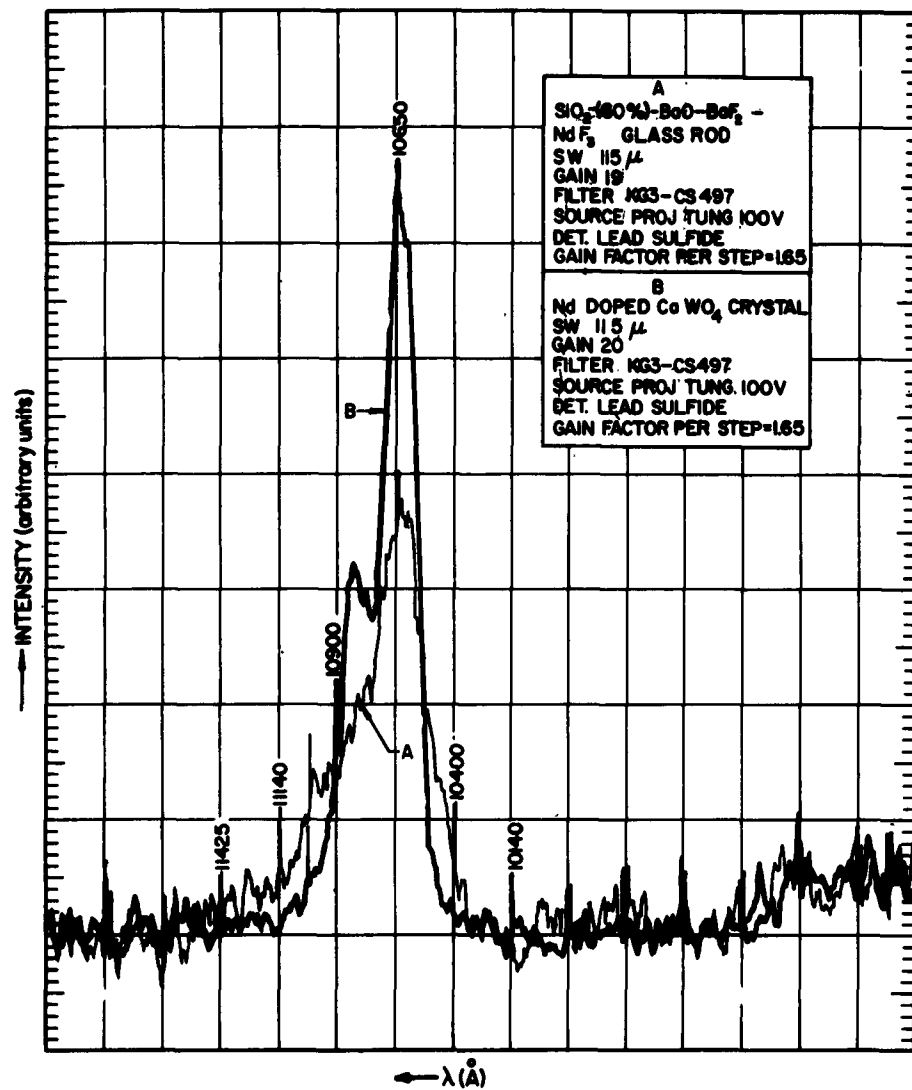
FIG. 5.2   EMISSION OF Nd^{+3} IN GLASS AND CaWO$_4$ CRYSTAL MATRICES - SLIT WIDTH 115μ.

was modified by replacing barium oxide and barium fluoride with calcium oxide and calcium fluoride. This glass crystallizes very readily and can not be used in this form. However, with the addition of small percentages of aluminium oxide as moderators, crystallization can be prevented. Also, by controlling the amount of aluminum oxide, the degree of crystallinity can be controlled.

By this means we have developed a glass host (i.e., glass No. 4) which when doped with neodymium fluoride shows high fluorescence. Fig. 5.3 compares the fluorescence emission of neodymium for glass No. 3 and No. 4. It can be seen that the fluorescence emission for glass No. 4 is a factor of three above that for glass No. 3. Decay time measurements for these glasses have been made and are shown in Fig. 5.4 as curves (a) and (b) for glasses No. 3 and No. 4, respectively. The decay time for glass No. 3 is 600μ seconds and that for glass No. 4 is 440μ seconds.

Laser rods fabricated from glass No. 3 doped with neodymium were tested for laser action and were observed to lase as discussed in the section on laser testing. Laser rods using glass No. 4 doped with neodymium are in process of fabrication and will be tested during the following period.

The host materials are being used for other rare earths in an effort to develop new lasers. During this period erbium was used as the dopant in glass No. 3. Fig. 5.5 shows the fluorescence emission line at 1.54μ for this sample. The line width is about 300 $\overset{o}{A}$ and the decay time (Fig. 5.4, curve C) is about 24 microseconds. Glass No. 4 will be used as the host in the following period and other rare earths will also be used.
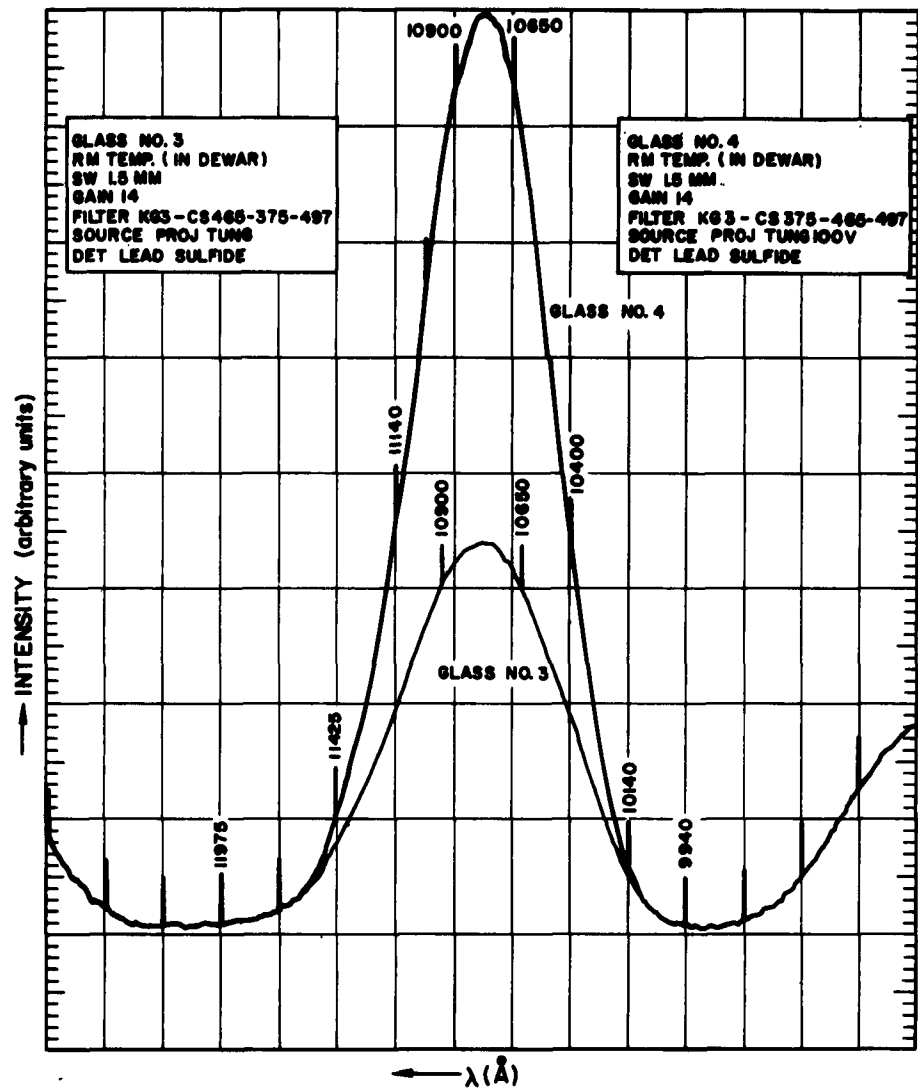
FIG. 5.3   EMISSION OF Nd^{+3} IN TWO GLASS MATRICES.

(a) Glass #3 Nd F_3

    Sweep speed 200 μsec/div
    approx decay time 580 μsec

(b) Glass #4 Nd F_3

    Sweep speed 200 μsec/div
    approx decay time 440 μsec
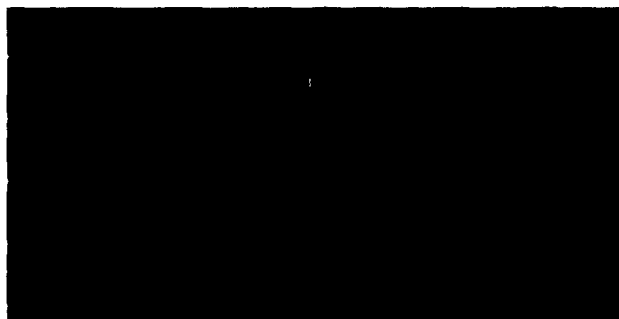
(c) Glass #3 ErF_3

    Sweep speed 20 μsec/div
    approx decay time 24 μsec
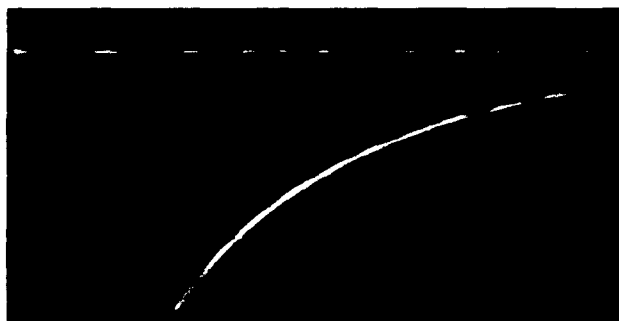
(d) Terbium F_3 AA μ crystals

    Sweep speed 100 μsec/div
    approx decay time 400 μsec

FIG. 5.4   DECAY TIMES OF LASER MATERIALS.

FIG. 5.5 EMISSION OF Er^{+3} IN GLASS NO. 3.

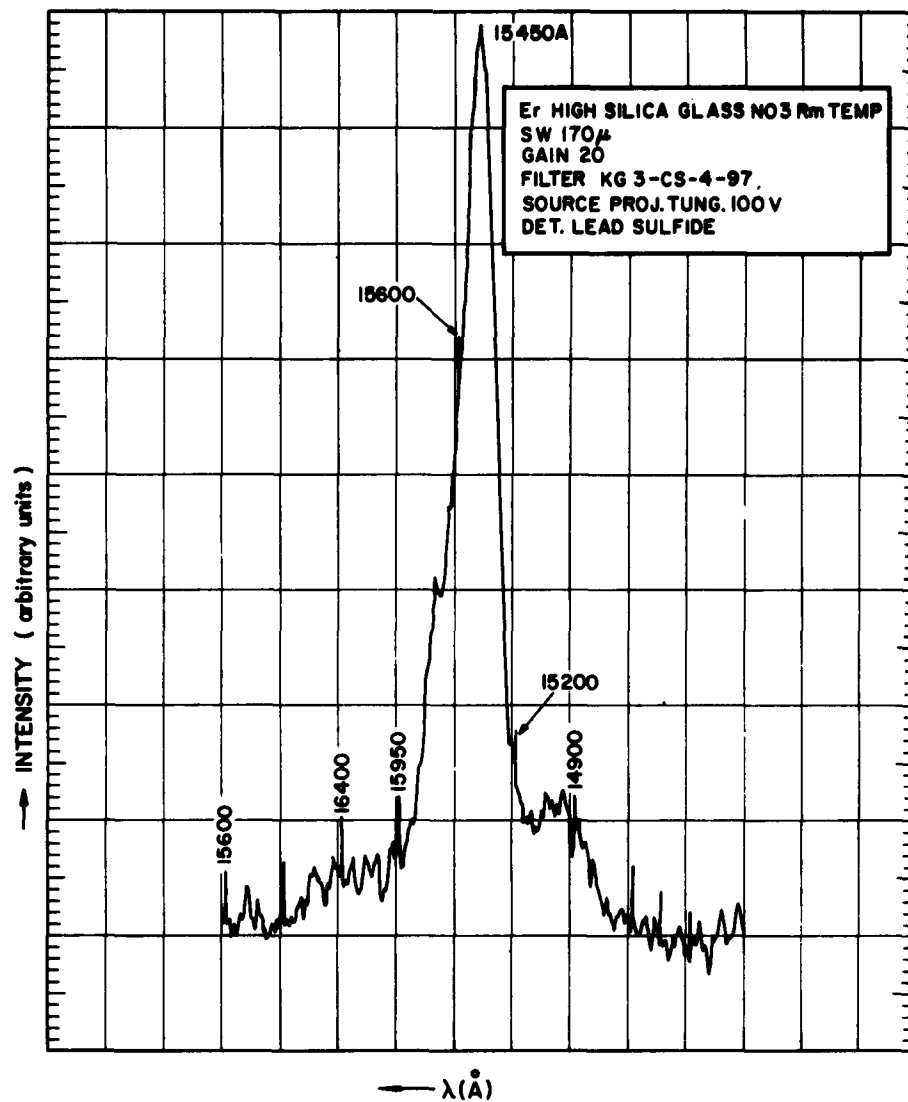6. LASER TEST METHODS AND LASER TEST

6.1 Laser Test Methods

Laser test facilities described in the previous report have been modified in the following ways. Part of this work has been done on other contracts but the test facility is made available for this program.

An optical bench making use of external confocal mirrors of the interference type has been constructed together with a laser housing and tested successfully with ruby, with and without Q-switching using a Kerr cell.

The laser housing is elliptical and is made to accommodate helical or linear flash tubes up to six inches in length. The length of the laser samples have been increased to four to six inches for better pumping and to make the end losses negligible.

The arrangement has been further modified so that this assembly can be cooled to about 10°C above liquid nitrogen temperature by the flow of dry gas cooled by liquid nitrogen. Protective measures have been taken so that condensation of moisture does not occur along the optical path and at the high voltage leads.

Previously it has been found that the laser rods of epoxy resin doped with chelates discolor or break when pumped with appreciable power. In order to increase the pump energy possible for these rods, filter arrangements have been made using a liquid filter to exclude as much of the unwanted light as possible. For the case of the epoxy resin rods of 1 mm in diameter clad with a Vycor capillary six inches long, we have been able to increase the pump power about five-fold without breaking. This design of laser rod is discussed in the section on plastic hosts along with other laser rod configurations.

6.2 Laser Test

Rods of neodymium doped glass No. 3 (described in a previous section) were drawn from a melt of the glass and fabricated into laser rods. These rods were doped with 2 percent neodymium and were about one-eighth inch in diameter and three inches long. When pumped with a Xenon flash tube, they were observed to lase as shown in Fig. 6.1. Fig. 6.1a already shows incipient lasering. Figs. 6.1c and 6.1d showing the full laser pulse is pumped at essentially the same energy with only the gain setting of the amplifier lower in d so that the full pulse can be seen.

A capacitance of $100\mu f$ was used at voltages indicated in the photographs. The fluorescence and laser output was observed by a photomultiplier with an S-1 surface together with an oscilloscope. The sweep speed is $100\mu sec/div$. The testing was done at room temperature and a helical flash tube was used. The resolution of the photomultiplier and cathode follower was such that the laser pulse is integrated into a single pulse. The threshold power for these rods is about 300 joules. However, it is to be noted that these rods were pulled by hand from a very small melt of glass (i.e., 40 cc platinum crucible). Thus, the result on threshold energy must be considered as preliminary. This work will be continued using glass No. 4 and other rare earths.

(a) Flash tube at 2.4 kv

　　Capacitance 100 µfd
　　Amp sensitivity 0.5v/cm
　　Sweep speed 100 µsec/div

　　Photomultiplier at 1 kv

(b) Flash tube at 2.8 kv

　　Capacitance 100 µfd
　　Amp sensitivity 0.5v/cm
　　Sweep speed 100 µsec/div

　　Photomultiplier at 1 kv

(c) Flash tube at 3.1 kv

　　Capacitance 100 µfd
　　Amp sensitivity 0.5v/cm
　　Sweep speed 100 µsec/div

　　Photomultiplier at 1 kv

(d) Flash tube at 3.2 kv

　　Capacitance 100 µfd
　　Amp sensitivity 2v/cm
　　Sweep speed 100 µsec/div

　　Photomultiplier at 1 kv

FIG. 6.1　OSCILLOSCOPE TRACE OF OUTPUT FROM NEODYMIUM
　　　　　DOPED GLASS LASER. DOPING LEVEL IS 2 PERCENT.
　　　　　HOST IS GLASS No. 3. LASER WAS OPERATED AT
　　　　　ROOM TEMPERATURE.

7. SUMMARY OF RESULTS

The results to date on metal organics for laser material have consisted of a survey of a large number of rare earth chelates of the beta-diketone derived type. These compounds were synthesized using various techniques and efforts were made to characterize these compounds and obtain compounds of high purity. Fluorescence emission measurements were made and used as a means of selecting promising compounds. During the past period our attention has been focussed on investigating the effects of the radicals associated with the beta-diketones on the fluorescence emission and lifetimes. To this end we have synthesized a number of chelates varying only the radicals used. Halogenation was used in a large part to make these changes. This was done because halogenation, in general, reduces non-radiative losses in the chelate by reducing the vibrational energy levels. Using a given rare earth, we have synthesized the acetylacetonate, the tri-fluoroacetylacetonate, the hexafluoroacetylacetonate, and others, as described in the text. To date we have found that the hexafluoroacetyl-acetonate, indeed, shows higher fluorescence intensity than the trifluo-roacetylacetonate, as can be seen by comparing Fig. 3.2 with Fig. 3.4. Also, it is very likely that purity has an effect on the intensity of fluorescence and efforts are being made to improve both synthesis methods and purification procedures for these relatively few compounds.

The work on glasses has proceeded to the point where a host mate-rial showing high fluorescence efficiency has been obtained as in glass No. 4. It is believed that these promising results are due to the use of fluorides instead of oxides and to the fabrication of glass that is more nearly crystalline rather than liquid as is the usual concept of optical glass. The formulation of this glass required procedures that

are in many ways alien to the usual concept of glass making such as rapid cooling and near crystallinity of the glass. A sample of neodymium doped glass (i.e., glass No. 3) showing about half the fluorescence intensity as glass No. 4 was observed to lase when pumped with about 250 joules at room temperature.

8. CONCLUSIONS

(1) The radicals used with the beta-diketone derived chelates have a definite effect on the fluorescence emission.

(2) Halogenation increases the fluorescence emission in some of our samples; however, the results are not uniform. It is believed that this is due to a non-uniform degree of purity of the samples.

(3) Fluorescence emission is reported for the chelates of neodymium, samarium, and terbium.

(4) A method has been developed for the successful doping of acrylic plastics with the rare earth chelates without quenching. These plastics have optical transmission further into the ultraviolet.

(5) A new glass host (glass No. 4) has been developed which shows fluorescence emission intensity about three times greater than our previous host (glass No. 3).

(6) A neodymium doped sampled of glass No. 3 was observed to lase when pumped with about 250 joules of energy.

9. RECOMMENDATIONS FOR NEXT INTERVAL

Approximately 68 percent of the technical effort has been completed, and the following program is recommended for the next quarterly period of the contract:

(1) Attempt to improve the purity of the beta-diketone derived chelates using samarium and neodymium as the rare earths with halogenated and other radicals as described in the text.

(2) Attempt to correlate the fluorescence emission and lifetime to the changes of radical and to the purity of the sample.

(3) Extend measurements to line widths and quantum efficiency.

(4) Make measurements to see if the rare earth ion can be seen in absorption through the ligand using samarium or other chelates. This will be done as a preliminary step to establish the possibility of studying stimulated absorption by spectroscopic means.

(5) Continue the work on glasses by fabricating laser rods of glass host No. 4 using neodymium and other rare earths as dopants.

(6) Continue attempts to improve the glass host with the objective of producing a c.w. laser.